# Conversion of biomass to fuel: Transesterification of vegetable oil to biodiesel using KF loaded nano-γ-Al₂O₃ as catalyst

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## ABSTRACT

KF-impregnated nanoparticles of γ-Al₂O₃ were calcinated and used as heterogeneous catalysts for the transesterification of vegetable oil with methanol for the synthesis of biodiesel (fatty acid methyl esters, FAME). The ratio of KF to nano-γ-Al₂O₃, calcination temperature, molar ratio of methanol/oil, transesterification reaction temperature and time, and the concentration of the catalyst were used as the parameters of the study. A methyl ester yield of $97.7 \pm 2.14\%$ was obtained under the catalyst preparation and transesterification conditions of KF loading of 15 wt%, calcination temperature of 773 K, 8 h of reaction time at 338 K, and using 3 wt% catalysts and molar ratio of methanol/oil of 15:1. This relatively high conversion of vegetable oil to biodiesel is considered to be associated with the achieved relatively high basicity of the catalyst surface (1.68 mmol/g) and the high surface to volume ratio of the nanoparticles of γ-Al₂O₃.

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## 1. Introduction

The synthesis of biodiesel (fatty acid methyl esters, FAMEs) from renewable biological sources, including animal fats and plant-based oils, has attracted considerable attention [1] and has the potential to replace a fraction of the petroleum diesel [2]. As shown by McNeff et al. [3] the economics of the biodiesel conversion processes would be attractive (i.e., commercially viable even in the absence of governmental subsidies) especially upon the conversion of waste oils, animal tallow and acidulated soap stocks to biodiesel.

There are four principal approaches to the synthesis of biodiesel involving the transesterification of the triglycerides of the plant oils and animal fats: base catalysis [4–7], acid catalysis [1,8–10], employing supercritical alcohol conditions [3] and enzyme catalysis [11–13]. The currently employed commercial processes rely on the transesterification of the triglycerides with methanol and homogeneous alkaline catalysts (NaOH or KOH). Since the biodiesel conversion efficiency depends on water and free fatty acid content, the current commercial facilities for biodiesel manufacture process only high purity virgin oils with negligible free fatty acid concentrations [3].

Homogeneous alkaline catalysts offer relatively short reaction times associated with their high catalytic activity but suffer from the difficulty of the separation of the catalyst from the glycerin phase, which renders them nonrecoverable and nonreuseable [3]. The use of heterogeneous catalysts that rely on the treatment of various catalyst supports, i.e., porous powders of zirconia, titania, alumina with Na, NaOH, KCl, K₂CO₃, KNO₃, KI, KBr, KF [14–18], offers various advantages including the recovery and recycling of the catalyst.

Alumina is commonly used as a heterogeneous catalyst support because of its high surface area, simple structure and availability. Kim et al. [14] have shown that γ-Al₂O₃ can be treated with Na/NaOH and can be used for the catalysis of the transesterification of soybean oil to biodiesel in conjunction with methanol and n-hexane to achieve a relatively high conversion of 94%. Xie et al. [17] have provided the procedures necessary for the manufacture of heterogeneous catalysts involving the impregnation of alumina with various potassium compounds (KI, KF, KOH, and KNO₃), followed by calcination. The catalysts of Xie et al. [17] have generated yields which are as high as 90% for the transesterification reactions of soybean oil.

To our knowledge, only one earlier study has focused on the use of nanoparticle-based catalysts for the transesterification of the triglycerides into biodiesel [19]. In the study of Reddy et al. nanocrystalline calcium oxides were used as the catalyst for the production of biodiesel via the transesterification of soybean oil and poultry fat with methanol at room temperature to generate

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a very high conversion of 99% [19]. The very high activity and surface reactivity of nanocrystalline calcium oxide were considered to be related to the high surface/volume ratio of nano-sized catalyst particles [19].

In the present study, nano-$\gamma$-Al$_2$O$_3$ (nano-alumina)-based heterogeneous catalysts were prepared and tested for the transesterification reaction of canola oil with methanol in a batch reactor system. The KF-treated and calcinated nanoparticle catalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and gas adsorption surface area analysis, BET, techniques. The basicity of the synthesized catalysts was determined using a Hammett indicator procedure [16–18]. The effects of KF over nano-$\gamma$-Al$_2$O$_3$ ratio, the reaction temperature and time, and methanol over oil and catalyst over oil ratios on the conversion rate of the triglycerides to biodiesel were investigated.

## 2. Experimental

### 2.1. Materials

The nano-$\gamma$-Al$_2$O$_3$ was obtained from Aldrich (designation 544833 with a reported particle size <50 nm). The water absorbance of nano-$\gamma$-Al$_2$O$_3$ was determined to be 0.5 g/g of nano-$\gamma$-Al$_2$O$_3$. KF (analytical-grade with a purity of 99.8 vol%) was supplied by Riedel-de Haën. The canola oil was purchased from a local food market. The free fatty acid content of the canola oil was determined to be 0.085 wt% following the AOCS Official Method Cd 3a-63 procedure [20].

### 2.2. Preparation of the heterogeneous catalyst

The KF loaded nano-$\gamma$-Al$_2$O$_3$ catalyst particles were prepared by the incipient-wetness impregnation method [21–23]. The incipient-wetness impregnation utilizes an amount of water that is less than or equal to that required to fill the pores of the support material. On the basis of the characterized water absorbance of nano-$\gamma$-Al$_2$O$_3$, a mixture of 0.12 g of nano-$\gamma$-Al$_2$O$_3$ and 1 mL of distilled water mixture was placed into a centrifuge tube, which was centrifuged at 1000 rpm for 2 min (another centrifuge tube with the same quantity of water was placed at the opposite side). Excess water on top of the alumina was removed and weighed. Water absorbance of alumina was determined from the difference of weights of wet and dry alumina. Aqueous solutions containing different concentrations of KF (10, 15, 20, 30 wt%) were prepared based on the water absorbance of the nano-$\gamma$-Al$_2$O$_3$. 4.25 g of nano-$\gamma$-Al$_2$O$_3$ was placed into a 250 mL flask held in an ultrasonic water bath. During impregnation vacuum was applied as the KF solution was pumped drop wise (using a peristaltic pump) onto the nano-$\gamma$-Al$_2$O$_3$. The nanoparticles, impregnated with KF, were dried in an oven at 393 K for 16 h. Upon drying, the nanoparticles were calcinated at three different temperatures of 673, 773 and 873 K for 3 h. Thus, the major parameters of the catalyst preparation procedure were the KF/nano-$\gamma$-Al$_2$O$_3$ ratio and the calcination temperature.

### 2.3. Characterization of synthesized catalysts

Nitrogen absorbance method using a multipoint BET sorptometer was used for the characterization of the adsorption and desorption isotherms and the determination of the BET surface area values of the synthesized catalysts. Prior to measurements, all samples were kept in an oven overnight under vacuum at 383 K.
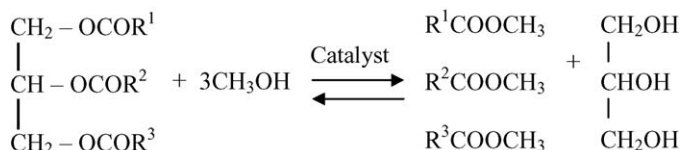
A Hammett indicator procedure, outlined in detail by Xie and Huang [18], was used for the characterization of the basic strength and basicity of the synthesized catalysts. This procedure involves placing about 300 mg of the sample into 1 mL solution of Hammett indicators diluted with 10 mL of methanol. Two hours were allowed to elapse for equilibrium to be reached under which no additional change of color took place. The basic strength is defined as being stronger than the weakest indicator, which exhibits a color change, and weaker than the strongest indicator that produces no color change. The following Hammett indicators were used: bromthymol blue ($H_-$ = 7.2), phenolphthalein ($H_-$ = 9.8), 2,4-dinitroaniline ($H_-$ = 15.0) and 4-nitroaniline ($H_-$ = 18.4). The basicity values (mmol/g) of the samples were determined by the method of Hammett involving the benzene carboxylic acid indicator (0.02 mol/L anhydrous ethanol solution) and titration until the color changed back to the original color [17,18].

X-ray diffraction analysis of all the synthesized catalysts was performed using a Rigaku/D/MAX 2200 diffractometer at room temperature. CuK$_\alpha$ radiation from a Cu X-ray tube running at 40 kV/40 mA was used in all samples. The Bragg angle range was between 5° and 75°. SEM of the KF loaded nano-$\gamma$-Al$_2$O$_3$ catalyst particles were obtained before and after transesterification using a Jeol_JSM_6400 Scanning Microscope. The elemental chemical analysis of the synthesized catalyst surfaces was carried out using the energy dispersive X-ray spectroscopy (EDS) technique. The mean values of the Al/K before and after the transesterification reaction were reported.

### 2.4. The transesterification of vegetable oil

The conversion of the vegetable oil to biodiesel, i.e., the transesterification reaction of the triglycerides to fatty acid methyl esters:

$$CH_2-OCOR^1 \qquad\qquad R^1COOCH_3 \qquad CH_2OH$$
$$CH-OCOR^2 + 3CH_3OH \xrightleftharpoons{\text{Catalyst}} R^2COOCH_3 + CHOH$$
$$CH_2-OCOR^3 \qquad\qquad R^3COOCH_3 \qquad CH_2OH$$

was performed in a jacketed 250 mL batch reactor equipped with a reflux condenser and a magnetic stirrer. The reactor was initially filled with 50 g of canola oil, which was heated to the reaction temperature while stirring at 600 rpm. The timing of the reaction was initiated as soon as the mixture of methanol and the catalyst was added into the reactor. The effects of the reaction temperature (298, 318, 333 and 338 K), molar ratio of methanol to oil (6:1–18:1), catalyst/oil weight ratio (1–7 wt%) and reaction time on the conversion of the triglycerides to biodiesel were investigated. All of the experiments were performed under atmospheric pressure. The typical experiment involved the collection of about 2–3 mL of sample from the reactor at hourly intervals. The conversions achieved were not affected by the rate of rotation of the stirrer in the 400–1000 rpm range and the rotational rate of the stirrer was kept constant at 600 rpm.

After the transesterification reaction the reaction mixture was poured into a separatory funnel where it was kept for 24 h. The biodiesel and glycerol layers exhibit different densities of 0.86 and 1.126 g/cm$^3$, respectively, and thus could be separated easily from each other.

Chemical analysis of the collected samples during the reaction and at the end of the completion of transesterification reaction was carried out using an Agilent 6890 gas chromatograph equipped with a flame ionization detector and a capillary column CARBOWAX 20M. The procedures for the determination of the fatty acid methyl ester concentrations followed European Standard of EN 14103 [24]. All data points reported are reproduced in triplicate and 95% confidence intervals, determined according to Student's $t$-distribution, are reported.
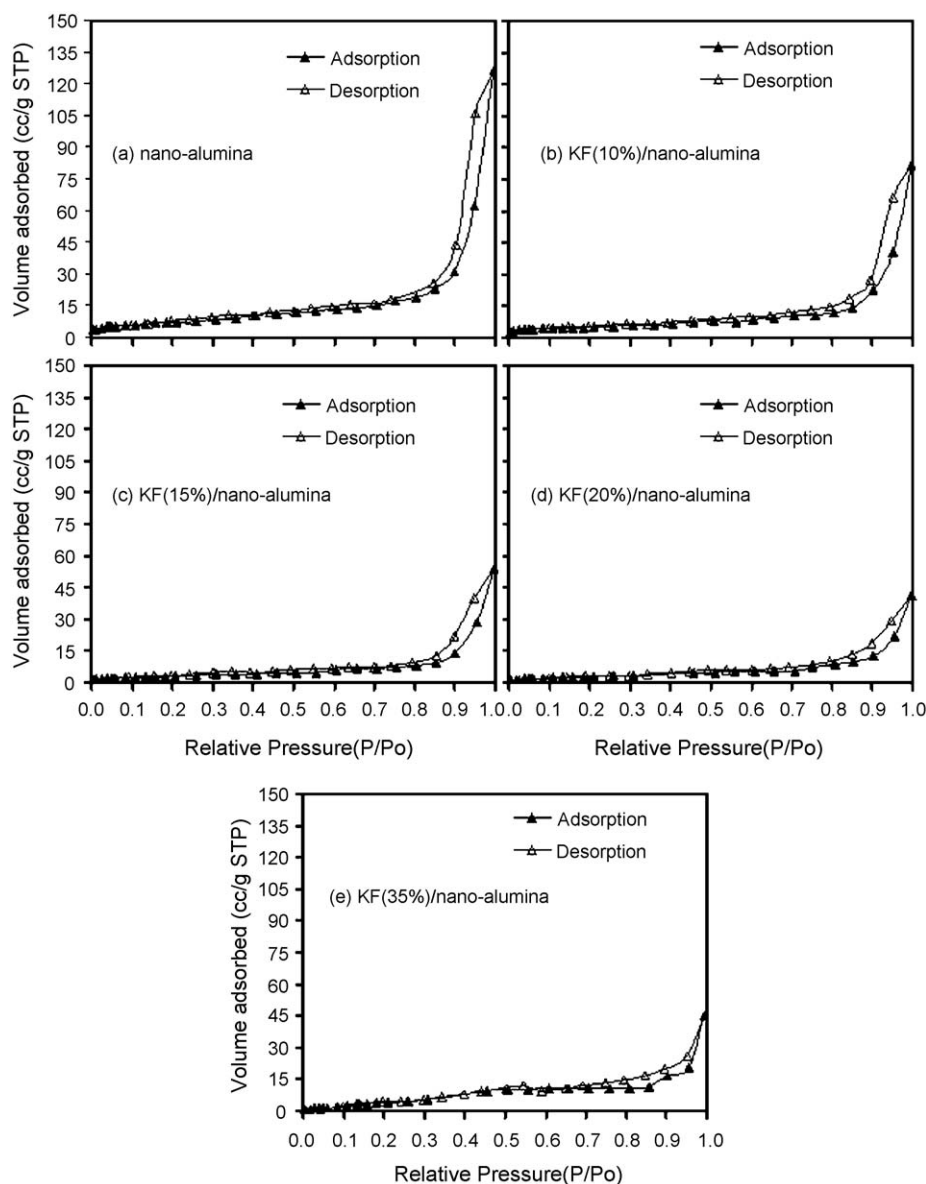
Fig. 1. Nitrogen adsorption–desorption isotherms of nano-alumina and potassium fluoride-impregnated nano-$\gamma$-Al$_2$O$_3$ catalysts.

## 3. Results and discussion

### 3.1. Catalyst characterization

The surface area, basic strength, basicity and the corresponding conversion to biodiesel values of the synthesized catalysts are reported in Table 1. The BET surface area of pure nano-$\gamma$-Al$_2$O$_3$ is $41.7 \pm 0.5$ m$^2$/g. Upon KF impregnation and calcination the BET surface areas of the $\gamma$-Al$_2$O$_3$ nanoparticles decrease, reflecting a significant reduction of the pore volume. The BET surface area value of the nano-alumina indicates that there is little porosity that penetrates into the body of the nanoparticles and that the pore volume resides at the surface of the nanoparticles. This is not surprising considering that as the size of the particle decreases the atoms at the surface occupy a significant volume fraction of the total volume of the particle. Nitrogen adsorption–desorption isotherms obtained with nano-$\gamma$-Al$_2$O$_3$ and nano-$\gamma$-Al$_2$O$_3$ catalysts impregnated with different concentrations of KF, following calcination, are shown in Fig. 1. The nitrogen adsorption isotherms of nano-$\gamma$-Al$_2$O$_3$ and the synthesized catalysts exhibited the typical Type III isotherm, to indicate that the KF-impregnated nano-alumina catalyst supports are macroporous and exhibit a low energy of adsorption [25]. The capillary condensation of N$_2$ was observed at the relative pressure range of 0.90 and 0.95. The pore size distributions of the materials that were used in this study are shown in Fig. 2. Most of the pores are in the 7–40 nm size range and the distributions are relatively narrow.

The transesterification of canola oil with methanol in conjunction with the synthesized nano-$\gamma$-Al$_2$O$_3$-based catalysts was carried out at 338 K for 8 h at a methanol/oil molar ratio of 15:1, 3 wt% catalyst. The corresponding values of conversion of triglycerides to biodiesel are shown in Table 1. The basic strength and the basicity values of various catalysts are also given. Basic strength values of the catalyst nanoparticles were invariant and were all in the 9.8–15 range; however, there were significant changes in basicity. Consistent with the earlier findings of Xie et al. [16,17], a strong correlation exists between the basicity values of the synthesized catalysts and their activities (Table 1), whereby the biodiesel yield increases monotonically with increasing basicity of the catalyst surface (over a constant reaction time of 8 h). The highest yield of FAME ($97.7 \pm 2.14\%$) was observed at a basicity of 1.68 mmol/g.

**Table 1**
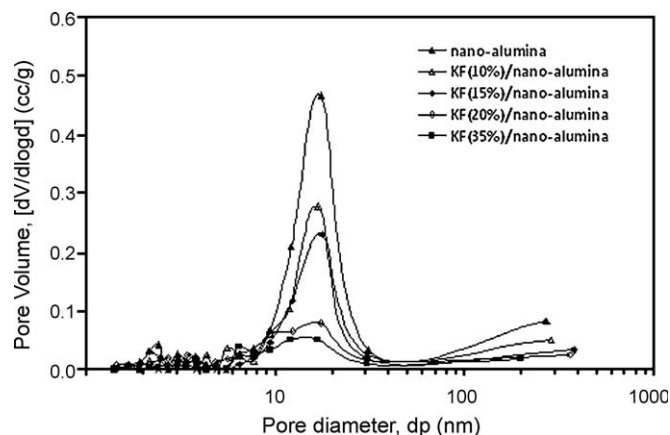Physical properties and catalytic activities of synthesized catalysts[a].

| # | Synthesized catalysts | Calcination temperature (K) | BET area (m$^2$/g) | Basic strength ($H_-$) | Basicity (mmol/g) | Biodiesel yield (%) |
|---|---|---|---|---|---|---|
| 1 | Nano-γ-Al$_2$O$_3$ | 773 | 41.7 ± 0.5 | <7.2 | – | No reaction |
| 2 | KF(10%)/nano-γ-Al$_2$O$_3$ | 773 | 17.5 ± 0.6 | 9.8–15.0 | 0.32 ± 0.05 | 82.1 ± 2.05 |
| 3 | KF(15%)/nano-γ-Al$_2$O$_3$ | 673 | 12.3 ± 0.6 | 9.8–15.0 | 1.04 ± 0.05 | 95.1 ± 2.85 |
| 4 | KF(15%)/nano-γ-Al$_2$O$_3$ | 773 | 11.8 ± 0.5 | 9.8–15.0 | 1.68 ± 0.05 | 97.7 ± 2.14 |
| 5 | KF(15%)/nano-γ-Al$_2$O$_3$ | 873 | 11.3 ± 0.5 | 9.8–15.0 | 0.72 ± 0.05 | 93.1 ± 1.78 |
| 6 | KF(20%)/nano-γ-Al$_2$O$_3$ | 773 | 11.1 ± 0.7 | 9.8–15.0 | 1.32 ± 0.05 | 96.8 ± 2.74 |
| 7 | KF(35%)/nano-γ-Al$_2$O$_3$ | 773 | 10.2 ± 0.5 | 9.8–15.0 | 1.31 ± 0.05 | 96.4 ± 1.56 |

[a] Reaction conditions: alcohol/oil = 15:1; reaction time: 8 h; catalyst amount: 3 wt%; 338 K.

The XRD patterns of nano-γ-Al$_2$O$_3$, KF-impregnated and calcinated catalysts are shown in Fig. 3. The X-ray diffraction pattern of KF-impregnated nano-γ-Al$_2$O$_3$ catalyst particles, following calcination at 773 K for 3 h, exhibited the characteristic peaks of nano-γ-Al$_2$O$_3$ ($2\theta$ = 37.0°, 46.0° and 67.0°) and KF ($2\theta$ = 20.0°, 29.0°, 33.0°, 48.0°, 56.0°, 60.0° and 71.0°). An additional K$_2$O phase appeared clearly in the diffraction patterns at the KF loading level range of 15 and 35 wt%. The peaks associated with the K$_2$O phase are observed at $2\theta$ = 30.0°, 42.7° and 53.0°. In the XRD pattern of catalyst particles with KF (10 wt%), K$_2$O formation could also be observed, although the intensities of these peaks were not as high as those observed for higher KF contents (15–35 wt%). Earlier studies have associated the high catalytic activity of KF-impregnated alumina catalysts with the basicity of the surfaces,

and related the basicity to the formation of the K$_2$O and Al–O–K groups (by the thermal decomposition of the loaded K compounds, and by salt–support interactions, respectively) [16,17]. As the KF loading is decreased there would be a reduction in the formation of the K$_2$O species and the Al–O–K groups which serve as the active sites for the transesterification reaction of canola oil with methanol, thus decreasing the yield.

SEM of nano-γ-Al$_2$O$_3$ (a), and the catalyst KF(15%)/nano-γ-Al$_2$O$_3$ before (b) and after transesterification reaction (first use) (c) and after transesterification reaction (second use) (d) are shown in Fig. 4. The primary particle sizes of the original nano-γ-Al$_2$O$_3$ and the synthesized catalysts are typically in the 10–50 nm range; however, some degree of agglomeration is also evident. The particle size distribution of the nano-γ-Al$_2$O$_3$ was not significantly altered upon the catalyst preparation, i.e., KF impregnation and calcination and upon the transesterification reaction (Fig. 4b–d, respectively).
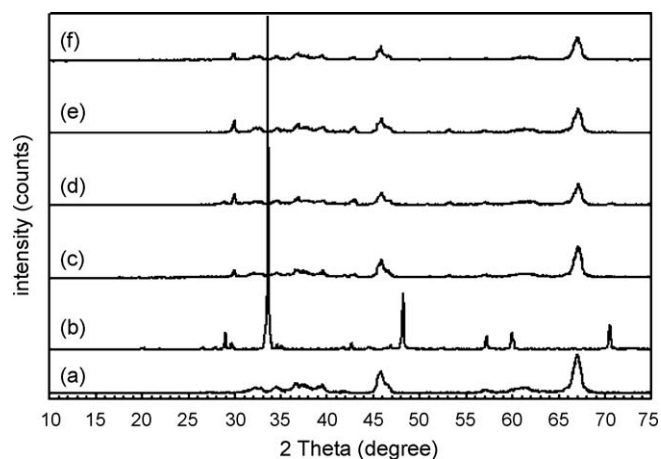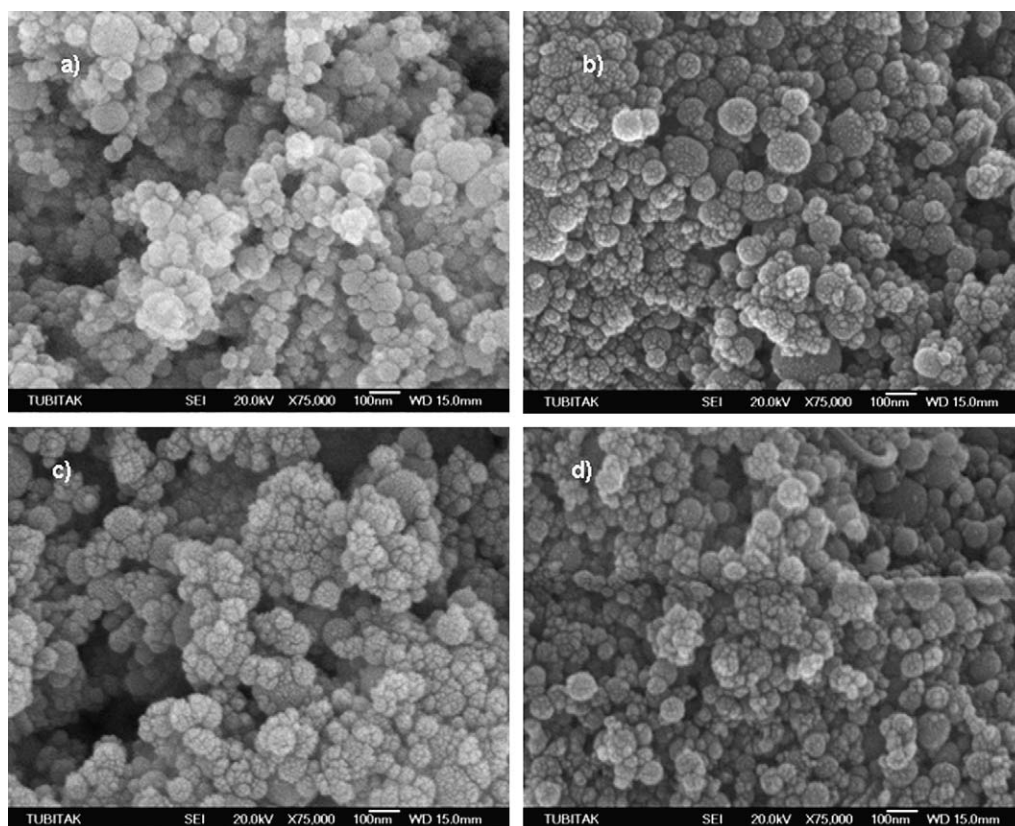
### 3.2. Effects of the parameters of the transesterification reaction

How do the parameters of the transesterification reaction affect the conversion of the oil to biodiesel in the presence of the catalyst nanoparticles? The variables that were investigated included the alcohol/oil ratio (mol/mol), temperature, time and catalyst amount (wt% of oil). The effects of the reaction time on conversion were characterized by collecting 2–3 mL of samples from the reactor on an hourly basis for chemical analysis (Fig. 5 shows conversion versus time). The biodiesel yield increased monotonically with time until a plateau in the conversion was achieved in about 7 h. It should be noted that this batch reaction rate is significantly smaller than the rates of biodiesel conversion achieved with a fixed bed reactor by McNeff et al. [3], i.e., the Mcgyan process which was able to generate biodiesel in seconds using a fixed bed reactor. Thus, there are significant additional gains to be made upon the better selection of reactor geometry, the catalyst configuration and the dynamics of mixing and diffusion in the reactor.

The stoichiometric molar ratio of alcohol to triglycerides that is required for the transesterification reaction is 3:1. However, previous studies have shown that higher molar ratios are necessary for the completion of the conversion of the triglycerides to fatty acid methyl esters [16–18]. Table 2 shows the dependence of the yield of fatty acid methyl esters on the methanol to oil ratio, which was varied in the range of 6:1–18:1. The other parameters, including the temperature of the transesterification reaction, the duration of the reaction and the catalyst amount, were kept constant at 338 K, 8 h and 3 wt% catalyst respectively. The catalyst used was KF(15%)/nano-γ-Al$_2$O$_3$. Methanol to oil ratios of 9:1 and higher all generated yields in the 93.5 ± 2.69–97.0 ± 1.59% range, generating a greater yield than observed at a methanol to oil ratio of 6:1 (at which the yield was only 82.5 ± 3.59%).

The typical dependence of the yield of the biodiesel to temperature for KF(15%)/nano-γ-Al$_2$O$_3$ catalyst at the molar methanol/oil ratio of 15:1 is shown in Fig. 6 (3 wt% catalyst and 8 h of reaction time). Consistent with the findings of the earlier



**Fig. 2.** Pore size distributions of nano-alumina and potassium fluoride-impregnated nano-γ-Al$_2$O$_3$ catalysts.



**Fig. 3.** XRD patterns of nano-γ-Al$_2$O$_3$, KF-impregnated and calcinated catalyst nanoparticles: (a) nano-γ-Al$_2$O$_3$, (b) KF, (c) KF(10%)/nano-γ-Al$_2$O$_3$, (d) KF(15%)/nano-γ-Al$_2$O$_3$, (e) KF(20%)/nano-γ-Al$_2$O$_3$, and (f) KF(35%)/nano-γ-Al$_2$O$_3$.

**Fig. 4.** SEM of nano–γ-Al$_2$O$_3$ (a), KF(15%)/nano–γ-Al$_2$O$_3$ prior to the transesterification reaction (b), KF(15%)/nano–γ-Al$_2$O$_3$ after transesterification reaction (first use) (c), and KF(15%)/nano–γ-Al$_2$O$_3$ after transesterification reaction (second use) (d).

studies on base catalyzed conversion of triglycerides to fatty acid methyl esters, FAMEs, the yield of FAMEs increased monotonically with increasing temperature, with the slope diminishing with increasing temperature (Fig. 6). The conversion values achieved for the first use of the KF(15%)/nano–γ-Al$_2$O$_3$ catalyst, i.e., 97.7 ± 2.14% are higher than what is reported by earlier studies on conversions achieved with alumina base catalysts for first usage [14–18]. The maximum conversion values achieved for first usage of the alumina base catalyst were 94% in Kim et al. [14] and 90% in Xie et al. studies [15–18]. This difference may be associated with the relatively high basicity and the important role played by the increasing surface to volume ratio of the catalyst particles, when the size of the catalyst is reduced to the nano-region.
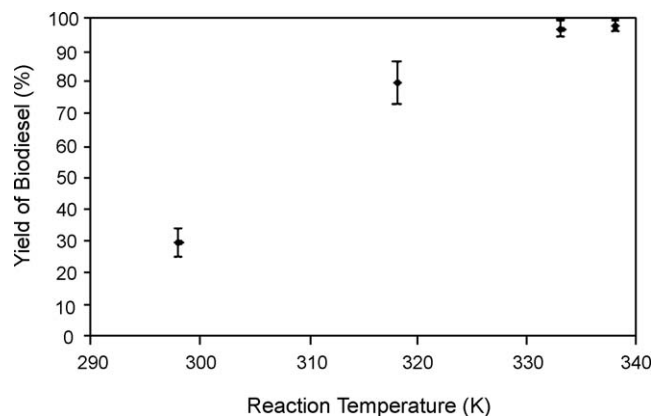
The typical dependence of the biodiesel yield on the catalyst amount (using KF(15%)/nano–γ-Al$_2$O$_3$ and at molar alcohol/oil

ratio of 15:1, 338 K and reaction time of 8 h) is shown in Fig. 7. The biodiesel yield reached a plateau value at a catalyst weight percent of about 2–3%.

The recovery and reuse of the catalyst is an important factor in the economics of the use of the heterogeneous catalysis process for biodiesel manufacture. Reusability of the KF(15%)/nano–γ-Al$_2$O$_3$ catalyst was tested by consecutively recovering and then reusing the catalyst nanoparticles up to three times. The transesterification reaction of oil with methanol was carried out repeatedly under one constant set of operating conditions (methanol/oil: 15:1, catalyst amount: 3 wt%; temperature: 338 K; reaction time: 8 h). Upon the completion of the transesterification reaction the catalyst nanoparticles were filtered out, recovered, placed into 10 mL of isopropyl alcohol and magnetically stirred for 1 h, filtered again
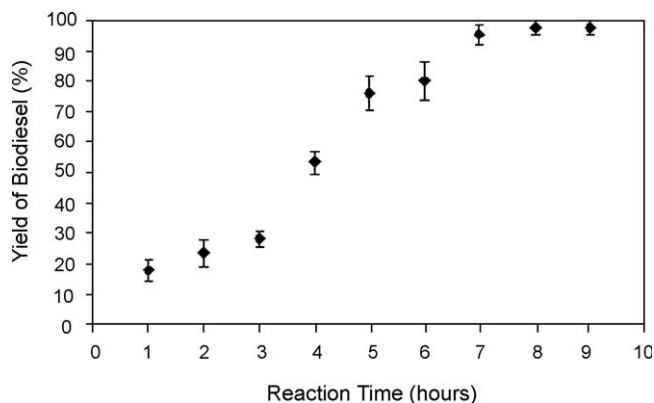


**Fig. 5.** Time dependence of the yield of fatty acid methyl esters, FAMEs, using KF(15%)/nano–γ-Al$_2$O$_3$ catalyst (alcohol/oil: 15:1, catalyst amount: 3 wt%, 338 K).



**Fig. 6.** Temperature dependence of the yield of fatty acid methyl esters, FAMEs, using KF(15%)/nano–γ-Al$_2$O$_3$ catalyst (alcohol/oil: 15:1, catalyst amount: 3 wt%, reaction time: 8 h).

**Table 2**

The effects of alcohol/oil ratio on the biodiesel yield upon the transesterification reaction[a].

| Runs | Methanol/canola oil (mol/mol) | Yield of biodiesel (%) |
|---|---|---|
| 1 | 6:1 | 82.5 ± 3.59 |
| 2 | 9:1 | 93.8 ± 2.69 |
| 3 | 12:1 | 94.9 ± 1.83 |
| 4 | 15:1 | 97.7 ± 2.14 |
| 5 | 18:1 | 97.0 ± 1.59 |

[a] Reaction conditions: catalyst: KF(15%)/nano-γ-Al$_2$O$_3$; reaction time: 8 h, catalyst amount: 3 wt%; 338 K.

**Table 3**

Basicity change of KF(15%)/nano-γ-Al$_2$O$_3$ catalyst upon reuse and potassium contents in ester and glycerin phases[a].

| # of usages | K content in ester phase (ppm) | K content in glycerin phase (ppm) | Basicity (mmol/g) | Yield of biodiesel (%) |
|---|---|---|---|---|
| Fresh | – | – | 1.68 ± 0.05 | – |
| First use | 550.3 | 2.6 | 0.31 ± 0.05 | 97.7 ± 2.14 |
| Second use | 5.3 | 0.5 | 0.30 ± 0.05 | 61.2 ± 3.85 |
| Third use | 5.2 | 0.5 | 0.30 ± 0.05 | 60.1 ± 2.76 |

[a] Reaction conditions: catalyst: KF(15%)/nano-γ-Al$_2$O$_3$; alcohol/oil = 15:1; reaction time: 8 h, catalyst amount: 3 wt%; 338 K.

and kept in a vacuum oven at 393 K for 16 h and then reused as the catalyst. As indicated in Table 3, the biodiesel yield was found to be 97.7 ± 2.14% (first use), 61.2 ± 3.85% (second use) and 60.1 ± 2.76% (third use).

The decrease in the conversion upon the reuse of the catalyst was consistent with the results of the EDS-based analyses of the γ-Al$_2$O$_3$ catalyst nanoparticles, which were carried out prior to and after the completion of the transesterification reaction. The EDS analysis indicated that the Al/K wt. ratio was 1.16 after KF impregnation but prior to the calcination and 1.32 after calcination and prior to the transesterification reaction. The Al/K wt. ratio decreased to 0.77 after the completion of the transesterification reaction for the first time. These results show that the heterogeneous nano-alumina catalyst has lost some of its active sites (as indicated by the 38% decrease of the conversion after the first run). The EDS results suggest that part of the K deposited on the fresh catalyst has leached during the first reaction run.

The leaching of K from the KF(15%)/nano-γ-Al$_2$O$_3$ catalyst into the ester and glycerin phases after the first, second, and the third reaction runs was documented by employing ICP Optical Emission Spectrometry (ICP-OES), following European standard of EN 14538 (Table 3) [26]. Three ICP-OES measurements were made for each case and the measurements were found to be subject to a standard error of about ±1%. The ICP-OES analysis indicated that approximately 550 ppm of K has leached into the ester phase during the first run of the reaction. The K content in glycerin phase was found to be 2.6 ppm after the first experiment. The K contents in the ester and glycerin phases determined after the second and third experiments were lower than those observed after the first experiment (Table 3). The values did not change after the second experiment.

Thus, part of the available K on the catalyst surface has leached from the nano-alumina support during the course of the first reaction, pointing to a lack of chemical stability of the fresh catalyst under the typical reaction conditions. This finding is further supported by the data presented in Fig. 5, where an induction period from a slow to a faster reaction rate was observed. The remarkable increase of the transesterification rates, observed after 3 h when the fresh catalyst was used, can be attributed to the presence of the leached and dissolved K in the reacting mixture which would act as a homogeneous catalyst. Basicities of the used catalyst particles decreased from 1.68 mmol/g to 0.31 mmol/g after the first reaction and remained constant thereafter.

The 2009 investigation of Benjapornkulaphong et al. [27] has also indicated that about 45 wt% of the K$_2$O leaches during the transesterification reaction and the reaction mainly proceeds through the conventional homogeneous catalysis, yielding relatively high methyl ester yields. The leaching of the K during the transesterification reaction thus mandates that the catalyst particles be retreated with KF prior to being recycled (again using impregnation with KF followed by calcination) as carried out by Xie et al. [28].
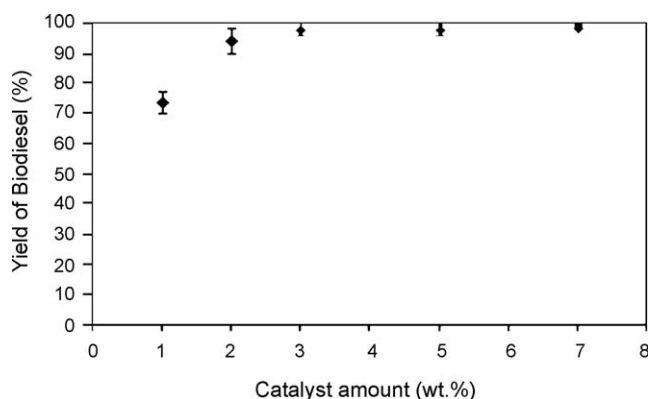
## 4. Conclusions

The effects of using a nano-sized alumina catalyst support on the transesterification of the triglyceride to fatty acid methyl esters, FAMEs, i.e., biodiesel, reaction were investigated in conjunction with canola oil and methanol in the 298–338 K range, under atmospheric pressure and using KF-treated nano-γ-Al$_2$O$_3$. The optimum loading amount of KF into nano-γ-Al$_2$O$_3$ was found to be 15 wt% and the highest basicity and the highest conversion of biodiesel were observed at a calcination temperature of 773 K. The conversion of the triglycerides to biodiesel reached values which were as high as 97.7 ± 2.14% and such high biodiesel yields reflect the benefits of reaching relatively high basicity and the use of nano-sized catalyst particles. Consistent with the findings of earlier studies [14–18,27,29] the basicity correlated with the biodiesel yield. The catalyst nanoparticles could be recovered and reused; however, part of the K initially deposited on the catalyst surface leached away from the support material during the course of the first reaction. The leaching of the K resulted in (30–40%) loss of catalyst activity, indicating that the catalyst surfaces need to be regenerated, i.e., reimpregnated with KF followed by calcination prior to recycling.

## Acknowledgement

**Fig. 7.** Dependence of the yield of fatty acid methyl esters, FAMEs, using KF(15%)/nano-γ-Al$_2$O$_3$ catalyst (alcohol/oil: 15:1, 338 K, reaction time: 8 h).

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